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BENZYL ALLYL STARCH AND OTHER MIXED
ALLYL STARCH ETHERS

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Introduction

Allyl ether of starch¹⁻⁴, which contains approximately 1.8 to 1.9 allyl

¹ P. L. NICHOLS, JR., R. M. HAMILTON, LEE T. SMITH, AND E. YANOVSKY. ALLYL ETHER OF STARCH. PREPARATION AND INDUSTRIAL POSSIBILITIES. *Ind. Eng. Chem.*, **37**, 201-2 (1945).

² E. A. TALLEY, R. M. HAMILTON, J. H. SCHWARTZ, C. A. BROWN, AND E. YANOVSKY. PREPARATION OF ALLYL STARCH. U. S. DEPT. AGR., BUR. AGR. AND IND. CHEM. *AIC-140*, (EASTERN REGIONAL RESEARCH LABORATORY) 5 PP. FEB. 1947. (PROCESSED.)

³ J. CHADAPAUX, G. CHAMPETIER, AND E. SAVOSTIANOFF, L'ALLYLAMIDON. *Bull Soc. Chim.*, **1948**, 185-90.

⁴ T. J. DIETZ, J. E. HANSEN, AND M. E. GALLAGHER. PROPERTIES OF ALLYL STARCH COATINGS. U. S. DEPT. AGR., BUR. AGR. AND IND. CHEM., *AIC-175*, (EASTERN REGIONAL RESEARCH LABORATORY) 8 PP., FEB. 1948. (PROCESSED.)

groups per glucose unit, has some outstanding properties as a coating material. Films made from solutions of this material dry tack-free in minutes. After a few weeks, the films become insoluble in all solvents; by the application of heat or by the addition of a paint drier, such as cobalt naphthenate or octoate, this insolubilization process may be greatly accelerated.

Because of their high resistance to organic solvents, allyl starch films are satisfactory for many uses. However, there may be some applications for which it is desirable to improve the resistance of the films to water or dilute aqueous solutions, such as dilute sodium hydroxide or dilute ethanol.

Improving the resistance of allyl starch to aqueous solutions is important, now that it has become commercially available⁵. This problem may be

⁵ ANONYMOUS. ALLYL STARCH: NEW PRODUCT DATA SHEET. REVISION D. GENERAL MILLS, INC., 11 PP., FEB. 1949.

attacked in at least three ways: The allyl starch may be mixed with some suitable hydrophobic material, it may be mixed with polymerizable materials which may or may not copolymerize with the allyl starch, or it may be allowed to react with compounds which will cover the remaining free hydroxyl groups. The last method is discussed in this article⁶. Several mixed

⁶ THE FIRST TWO METHODS ARE BEING INVESTIGATED IN THIS LABORATORY.

ethers of allyl starch were prepared, and films made from them were tested for resistance to various reagents. The most intensive study was made on benzyl allyl starch.

Preparation and Testing of Films

The mixed ethers were dissolved in a solvent, usually toluene. In some cases, when turbid solutions resulted, clarification was effected by adding a small amount of a polar solvent. Polar solvents were added sometimes to decrease the viscosity of the solution or to give a smoother film. Most of the solutions had a solids content of 40-45 percent and a viscosity of approximately 1 to 2 stokes. All solutions used for testing were clear and water-free. Films were poured on glass plates, and when tack-free were heated for various periods of time in a forced-draft oven at 100° or 150° C. The cure was determined by the following three tests⁷. The spot test is

⁷ THE CURE AS DETERMINED BY THESE METHODS IS NOT NECESSARILY THE OPTIMUM FOR PRACTICAL PURPOSES.

made by placing a drop of malachite green (0.06 percent solution in 50/50 acetone-acetic acid) on the film and allowing it to dry. If the spot washes off in running water, a cure is indicated. In the flat-knife test, an attempt is made to lift a portion of film by running the edge of a sharp knife or razor blade between the film and the glass. The edge knife test is made by drawing the edge of the knife across the film in the direction of the length of the blade, with the blade almost perpendicular to the film. In either test, if the film flakes off it is cured; if it comes off in curled strips it is not cured. After the time for curing was determined, test tubes were dipped in the solutions of the mixed ethers. About 4 inches of each tube was coated by means of a dip-coater having a withdrawal rate of 2 inches per minute. The films were then cured in the forced-draft oven for the proper time.

The coated tubes were suspended in the testing reagents in such a way that approximately half the film was immersed in the liquid. The condition of the films was noted at intervals.

Table I shows the results of some tests on allyl starch itself, which are included for comparison with tests on the mixed ethers. Unless otherwise indicated, the time listed in the table is the time at which the film failed. Zero time indicates that the film failed in less than 3 minutes. A range (maximum and minimum time of failure) is given in cases in which the test results were too indefinite or the number of observations too few to show a more definite time of failure. The films were considered to have failed if they were broken at any point or if a large area became swollen, wrinkled, or blistered. The symbol "g" indicates that there was no sign of attack on the film at the time listed. The symbol "w" means that the film was wrinkled or blistered to a small extent but recovered after being removed from the reagent, that is, the film became smooth again and still adhered to the glass. Films which were wrinkled or blistered to a small extent but which did not recover fairly well are listed as having failed.

This method of recording results was used also in Tables II to VI. Batches listed on more than one table are given the same number in each case.

Discussion of Results

Effects of Substituent Groups. Table II lists batches of benzyl allyl starch of various degrees of substitution. Although the results are not always clear-cut, in general these films showed greater resistance to aqueous reagents than films of allyl starch (Table I), especially when cured at 150° C. and when highly substituted. The tendency of films of allyl starch and allyl starch mixed ethers to have greater resistance when cured at 150° than at 100° C. was more pronounced in benzyl allyl starch.

The other mixed ethers of allyl starch (Table III) did not show any definite improvement over allyl starch.

The curing time for most of the mixed ethers was about the same as for allyl starch. However, the chlorobenzyl allyl starches and a few batches of benzyl allyl starch required two to four times as long.

Effects of Other Variables. Table I indicates that it was difficult to get reproducible results on different batches of allyl starch. The same difficulty occurred with the mixed ethers of allyl starch. Several factors may be responsible for variations in the test results, namely, differences in substitution, molecular weight, and molecular weight distribution. Also some variable in the testing conditions might be a factor. It was noted that a great many film failures occurred in curved portion at the bottom of the test tube. Either mechanical defects are more prevalent in this section or the film has a different thickness because of improper drainage of the solution and is therefore cured to a different degree. For this reason, a study was made on allyl starch in which some of the films were protected by a cap of paraffin on the bottom and a narrow band of paraffin around the upper edge. The cylindrical portion of the film was left exposed. Of the 66 comparative tests made (Table IV), the protected film in 36 had more resistance; in 7 it had less; in 4 cases there was no appreciable difference; and in 19 the results were indeterminate. The tests show, therefore, that the upper edge and the curved surface of film were more susceptible to attack. On the other hand, it should not be concluded that the films are necessarily poor on curved surfaces. It is believed that properly plasticized films applied by brushing or spraying would be more uniform and not show this defect.

To ascertain the effects of plasticizers, benzyl allyl starch films plasticized with Paraplex RG7⁸, Duraplex ND75⁸, and Arochlor 1242⁹ were tested

⁸ RESINOUS PRODUCTS & CHEMICAL CORPORATION, PHILADELPHIA, PENNSYLVANIA

⁹ MONSANTO CHEMICAL COMPANY, ST. LOUIS, MO.

for resistance ¹⁰. Table V shows ¹¹ the results. Films plasticized with

¹⁰ THE MENTION OF COMMERCIAL PRODUCTS DOES NOT IMPLY THAT THEY ARE INDORSED OR RECOMMENDED BY THE DEPARTMENT OF AGRICULTURE OVER OTHERS OF A SIMILAR NATURE NOT MENTIONED.

¹¹ THE AUTHORS ARE INDEBTED TO A. N. WRIGLEY AND J. SICILIANO FOR THESE DATA.

Duraplex ND75 showed considerable improvement in resistance to most of the reagents; an adverse effect was noted with phenol and sodium hydroxide. The other plasticizers, however, gave almost as many cases of decreased resistance as of improved resistance. Duraplex also imparted greater hardness and elongation to the films than did the other plasticizers.

Another study was made of the effect of the degree of cure on the resistance of films to solvents (Table VI). At least in the case of allyl starch, more highly cured (or overcured) films had greater resistance to acetone, dilute phenol, and dilute ethanol than films just cured or somewhat undercured, as determined by our tests. On the other hand, in most cases too great an overcure lessened the resistance of films to dilute ammonia. One batch of allyl starch (No. 52) and the benzyl allyl starch (Batch No. 46) showed more resistance to dilute alkali when undercured. However, the cured films of the other allyl starch batch tested (No. 51) were more resistant to alkali.

In light of the above discussion, it should be borne in mind that the tests are intended to give only a comparison of the various ethers when films are prepared and cured under a particular set of conditions. They do not indicate the solvent resistance that may be achieved by special compounding or by altering the conditions of cure. In some cases overcuring improves solvent resistance. In others, undercuring might result in improvement.

Preparation of Mixed Ethers of Allyl Starch

Preparation of certain mixed ethers of allyl starch has been reported^{1,2}.

^{1,2} R. M. HAMILTON AND E. YANOVSKY, MIXED ALLYL ETHERS OF STARCH, *Ind. Eng. Chem.*, **38**, 864.6 (1946); U. S. PATENT No. 2,463,869, MARCH 8, 1949.

Besides testing the products, one purpose in continuing this work was to use or develop methods of preparation which would be more economical.

The method of preparing benzyl allyl starch was similar to that used for allyl starch². When allyl chloride was used, the reaction was carried out in an autoclave. Nine-tenths mole of benzyl chloride and either three or four moles of allyl chloride per mole (anhydroglucose equivalent) of starch were used. With allyl bromide, the ether was prepared in a flask. Four moles of allyl bromide was used per mole of starch. In all cases, the amount of sodium hydroxide used was equivalent to 95 percent of the total amount of halide present. The sodium hydroxide was added as a solid, as a 50 percent solution, or as a combination of both. Acetone was used as a solvent in the autoclave batches; toluene or methyl ethyl ketone was used for the others. In some of the autoclave batches, sodium iodide, (2 percent on the weight of dry starch) was used as a catalyst. Either the allyl chloride and benzyl chloride were added together, or one was added after the reaction mixture had been heated for some time. In general, the starch was slurried in one or both halides, and then cooled 50 percent sodium hydroxide solution was added, and the mixture was stirred for half an hour, with cooling. The remaining reagents, including any solid sodium hydroxide, were then added, and the mixture was heated to the reaction temperature. After the reaction had taken place, the product was solubilized by heating it with acid.

A typical batch (No. 14) was prepared as follows: 932 grams of air-dry potato starch (13 percent moisture) was placed in a 2-gallon glass-lined autoclave and slurried with 1148 grams of allyl chloride. Fifty-percent sodium hydroxide solution (1380 grams) and 18 grams of sodium iodide were then added, and the mixture was stirred for half an hour, with cooling. After this, 51 grams of solid sodium hydroxide and 4 liters of acetone were added, and the mixture was heated for 3-1/4 hours at 90° C. Next 570 grams of benzyl chloride was added, and heating was continued for 7-1/2 hours. The batch was then acidified with 60 ml. of concentrated hydrochloric acid (to pH 2) and heated at 90° C. until it had gone into solution.

Some lachrymatory substance (possibly benzyl bromide) was noted in benzyl allyl starch prepared with allyl bromide. This was not present when allyl chloride was used.

Table VII lists the batches of benzyl allyl starch made by the general procedure described above. In the flask batches, 632 grams of air-dry potato starch (13 percent moisture) and 4 moles of allyl bromide per mole of starch were used. In the autoclave batches, 932 grams of starch was used. The second column of the table lists the amount of sodium hydroxide added as a solid; the remainder of the sodium hydroxide was added as a 50-percent solution. In batches 1 to 3, 1250 ml. of toluene was used as solvent; in batches 4 and 5, 1250 ml. of methyl ethyl ketone was used, and in batches 6 and 7 a mixture of 1000 ml. toluene with 500 ml. benzene. The other batches were made with 4 liters of acetone. Sodium iodide was used in batches 14 to 23.

Analyses of batches 8 to 12 indicate that reducing the amount of water in a batch causes an increase in allyl content. It is also apparent from Table VII that the smaller proportion of allyl chloride produces a slightly smaller total substitution in spite of the use of sodium iodide as a catalyst. The preliminary samples taken show that in many cases the reaction was almost complete in about half the reaction time.

There were also a few batches in which special methods were used to achieve a high substitution. Usually in these cases benzyl allyl starch of ordinary substitution was first isolated, then further allylated or further benzylated. Allyl bromide and sodium hydroxide were added in portions, the latter mostly as solid. Batch 47 (Table II) was produced in this manner by further allylation. Batch 45 was prepared by further allylating batch 10; batch 46 was prepared by further benzylating batch 10. In one batch (not tested because of insufficient material) a substitution of 0.22 benzyl and 2.29 allyl groups per anhydroglucose unit was obtained by first preparing benzyl starch and then allylating in the manner described above.

Even these special methods did not produce complete substitution. However, this was not unexpected, considering the well-known difficulty of completely etherifying starch.¹³

¹³ W. N. HAWORTH, E. L. HIRST, AND J. I. WEBB. POLYSACCHARIDES. PART II. THE ACETYLATION AND METHYLATION OF STARCH. *J. Chem. Soc.*, 1928, 2681-90.

On the basis of the process used here, a materials cost of 32 cents per pound was estimated for benzyl allyl starch, as compared with a materials cost of 25 cents per pound for allyl starch.

The other mixed ethers of allyl starch (Table VIII) were prepared by methods similar to those used in making benzyl allyl starch. In general, the starch was mixed with a solvent, sodium hydroxide (as a 50-percent solution or a combination of solid and solution), and 1 to 2 moles of alkyl halide per mole (anhydroglucose equivalent) of starch. After the mixture was heated for a few hours, 4 moles of allyl bromide were added, and the reaction was continued. Allyl chloride was used in the autoclave batches (Nos. 27 to 31 and 39) - 3 moles in batches 27, 30, and 31, and 4 moles in batches 28 and 29; batches 32 and 34 used 13 moles of allyl bromide, and batch 33 used 20 moles. In batches 27, 30, and 31, the ethyl chloride was not added until a few hours after allylation was started. Sodium iodide was used as a catalyst in several batches (Table VIII). In batch 37, an amount of sodium iodide equivalent to the butyl chloride was used. The butyl chloride and sodium iodide were heated together in methyl ethyl ketone for 8 hours before the starch and alkali were added.

Of the organic chlorides used, the benzyl and *o*- and *p*-chlorobenzyl chlorides were the most reactive, having a reactivity comparable to that of allyl chloride. The alkyl chlorides, especially the butyl and amyl chlorides, were considerably less reactive.

Yields of benzyl allyl starch and ethyl allyl starch were generally close to 100 percent of theoretical. The chlorobenzyl allyl starch derivatives were obtained in 90 percent yield. Yields of butyl allyl starch ranged from poor to very good. Yields of amyl allyl starch averaged about 54 percent.

The allyl starch mixed ethers differed somewhat in solubility from allyl starch itself. They were usually completely soluble in both acetone and toluene. They were also more intolerant to water in the solvent than was allyl starch. A small amount of water kept the allyl starch derivative from dissolving in acetone or caused the formation of a two-phase solution.

The number of allyl and hydroxyl groups per glucose unit was found by direct determination; the degree of substitution of the other substituent was obtained by difference. The analytical samples were prepared as described by Hamilton and Yanovsky¹². Unsaturation was determined by the Wijs method¹². The method of hydroxyl determination was essentially that of Malm, Genung, and Williams¹⁴, except that acetone instead of water was

- 14 C. J. MALM, L. B. GENUNG, AND R. F. WILLIAMS, JR., ANALYSIS OF CELLULOSE DERIVATIVES, DETERMINATION OF FREE HYDROXYL CONTENT, *Ind. Eng. Chem., Anal. Ed.*, 14, 935.40 (1942).

used as a solvent and washing agent. This prevented the precipitation of the acetylated sample in coarse lumps.

Summary and Conclusions

Various mixed ethers of allyl starch were prepared, namely, ethyl, butyl, amyl, benzyl, *o* - chlorobenzyl, and *p* - chlorobenzyl allyl starch. Films made from these compounds were compared with allyl starch films for resistance to 10 percent ammonia, 5 percent sodium hydroxide, 5 percent phenol, 50 percent ethanol, 4 percent acetic acid, and undiluted acetone. A few tests were made also with 1 percent soap solution and boiling distilled water.

Benzyl and chlorobenzyl allyl starch were easier to prepare than the other allyl starch mixed ethers because of the greater reactivity of the benzyl and chlorobenzyl chlorides, which compare in reactivity with allyl chloride. The purely aliphatic chlorides were much less reactive under the conditions used.

Benzyl allyl starch when cured at 150° C. showed marked improvement over allyl starch in resistance to aqueous solvents. This refers not only to the highly substituted benzyl allyl starch made by the special methods described but also to that of ordinary substitution made by more practicable methods. The other mixed ethers showed no definite improvement over allyl starch. Benzyl allyl starch, then, because of ease of preparation and the solvent resistance of its films, gives most promise of being a compound suitable for further development.

These conclusions are based on unmodified films tested under a particular set of conditions. Better results might be obtained with properly plasticized films applied and cured under the optimum conditions for the use to which they are intended.

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TABL. I

Resistance of Allyl Starch Films to Various Reagents

Batch No.	Substitution Allyl Groups per Glucose Unit	Viscosity	Solids	Curing Time	Contact Time (hours) Before Failure ¹							Boil- ing Water		
					Stokes	% Hours	10% Am- monium Hydroxide	5% Sodium Hydroxide	5% Phenol	50% Ethanol	4% Acetic Acid		Acetone	1% Soap Solution
Films Cured at 100° C.														
53 ²	1.81	0.9	43	5	0	0	1.3	0.3	72w					
52 ³	1.82	1.5	40.5	2	2.5, 1 ⁴	8.5 - 18	2.5-8.5	1.7, 1.2 ⁴	2.5-8.5	2.5-8.5	8.5-72			
51	1.78	4.4	40	3	.7	.8	.5	1.1	72g	3	72g ⁵	0		
Films Cured at 150° C.														
Min.														
53 ²	1.81	.9	43	20	.1	.1	.1	0.8	18.3			0		
52 ³	1.82	1.5	40.5	20	.7	3-18	4	4-19	72g	4 - 19	72g	.2		
51	1.78	4.4	40	20	2.3	17.5-20	7.8-17.5	2-4.3	114g	7 - 17	114g	.1		
54	1.80	1.0	40	20	0	0	.3	0.7	28.5	77g		0		

¹ g indicates that the film had not been attacked; w indicates that the film wrinkled but recovered.

² Allyl starch solution supplied by General Mills, Inc.

³ Allyl starch solid supplied by General Mills, Inc.

⁴ Check sample.

⁵ Slight separation of the film from the tube noticed after removal from the testing reagent.

TABLE II

Resistance of Benzyl Allyl Starch Films to Various Reagents

Batch No.	Substitution Groups per Glucose Unit		Curing Time Hours	Contact Time (hours) Before Failure ¹						
	Benzyl	Allyl Hydroxyl		10% Am- monium Hydroxide	5% Sodium Hydroxide	5% Phenol	50% Ethanol	4% Acetic Acid	Acetone	Boiling Water
Films Cured at 100° C.										
5	0.35	1.89	0.76	2.5	0.6	2	0.4	1.1	0.7	0.5
8	.46	1.85	.69	17	.1	.1	.6	5-24	5g, 72w	1.8
10	.57	1.69	.74	21	.1	.1	.4	2.5-18.5	72g	2.5-18.5
45	.49	2.14	.37	5	.5	.1	.6	48g, 72w	72g	72w
46	.96	1.61	.43	24	.5	.3	.4	73g	73g	1.1
47	.96	1.70	.34	4	120w	72w	.2	.8g, 120w	1	
Films Cured at 150° C.										
Min.										
48	.48	1.81	.71	40	72g	72w	.8	58		
5	.35	1.89	.76	15	24	72g	3.3	1.8	72g	1.9
8	.46	1.85	.69	30	1	4	.8	5	75g	4.3
10	.57	1.69	.74	70	1	.7	1.7	72g	72g	2.5
45	.49	2.14	.37	40	.5	.6	2	27g, 67	72g	1.2
46	.96	1.61	.43	90	72w	.8-1.8	.8-1.8	72g	72g	6-22
47	.96	1.70	.34	20	72w	72w	.9	72w		

¹ g indicates that the film had not been attached; w indicates that the film wrinkled but recovered.

TABLE .11

Resistance of Films of Allyl Starch Ethers to Various Reagents

Batch No.	Substituent (R)	Substitution Groups per Glucose Unit		Curing Time	Contact Time (hours) Before Failure ¹							
					Hours	10% Ammonium Hydroxide	5% Sodium Hydroxide	5% Phenol	50% Ethanol	% Acetic Acid	Acetone	Boiling Water
Films Cured at 100° C.												
24	Ethyl	0.78	1.77	0.45	5	0.4	3.3g; <67	3	1.6	72g		0.2
25	Ethyl	.74	1.77	.49	5.3	.1	.1	0.1	.1-0.8	6.3-47	26 - 48	
36	Butyl	.39	2.07	.54	2	.2	1.2	.8	1.4	72		.7
49	Butyl	.13	2.05	.82	5	.2	1	.4	1.2	1.2g, 70w	.4	
50	Amyl	.16	2.34	.50	4	.1	.4	.5	.6-2	.6-2	2 - 4	0
43	o-Chloro-benzyl	.54	1.79	.65	16	.3	0	1.4	5.8	6.3g, 46w	6 - 23	
44	p-Chloro-benzyl	.58	1.77	.69	17	.1	0	.5	1.2g, 53w	22g, 70w	30g, 73w	
Films Cured at 150° C.												
24	Ethyl	.78	1.77	.45	20	<72 ²	<72 ²	.6	2.8	72g		2.5
25	Ethyl	.74	1.77	.49	15	.2	.1	.5	.5	5g, 72w	23	.2
26	Ethyl	.76	1.73	.51	40	0	.1	.3	1	30 - 46		
36	Butyl	.39	2.07	.54	10	0	0	1	1.8	44		
49	Butyl	.13	2.05	.82	15	1	.4-21	1-3	5-21	72g	<19	3
50	Amyl	.16	2.34	.50	15	1	.2-3	1-3	1-3	72g	6-21.5	0
41	Amyl	.42	2.31	.27	30	.1	.1	2	6-21.5	30-41		
43	o-Chloro-benzyl	.54	1.79	.65	60	.3	1.8	1.8	6-23	74g	46	
44	p-Chloro-benzyl	.58	1.77	.69	40	.8	0.1	74g	1.3	74g	.7g, 74w	

(Continued)

Table III - continued

- 1 g indicates that the film had not been attacked; w indicates that the film wrinkled but recovered.
- 2 Completely wrinkled in 31 minutes. Fractured when removed from testing reagent at end of 72 hours.

TABLE IV

Effect of Protecting Allyl Starch Films with Paraffin

Contact Time (hours) Before Failure ²								
Curing Temp. (° C.)	Curing Time ¹ Hours	10% Am- monium Hydroxide	5% Sodium Hydroxide	5% Phenol	50% Ethanol	"% Acetic Acid	Acetone	1% Soap Solution
Batch 51								
100	2	0	0	0.2	0.3	7.5-20	1	2-6
100	2p	.3	.1	.7	3.2	72g	2.3-72	50-58
100	4.5	0	.1	.2	2	.4	72g	.4
100	4.5p	.2	.1	2-6	2-6	2	72g	42-68
100	6	.1	.9	9.8-19	9.8	9.8-19	72g	64-72
100	6p	.2	.5	3.3	1.5	2.7	72g	52-58
Mins.								
150	10		2					
150	10p		72g					
150	50	.3						
150	50p	.1						
150	100	.3						
150	100p	1.5						
Batch 52								
Hours								
100	1	8.5-18	2.3	.3	.8	8.5-72	.2	8.5-72
100	1p	8.5-72	2.9 ⁴	.5	1.3	72w	.3	18-72
100	2	2.5, 1 ⁵	8.5-18	2.5-8.5	1.7, 1.2 ⁵	2.5-8.5	2.5-8.5	8.5-72
100	2p	8.5-72	26.5-42	2.5-8.5	2.5	2.5	2.5	25-72
100	4	2.3	2.5-8.5	8.5-18	2.3	2.5-8.5	26.5-42	8.5-42
100	4p	8.5-42	26.5-42	8.5-18	8.5-18	2.5-8.5	26.5-42	8.5-72
100	6	.1	.7	2.8	2.8	.8	46-51	1.8
100	6p	4.1	6.21	.1	6	30-72	6-21	72w
Mins.								
150	10	.7	4-19	.7	.5	72w	.7	72w
150	10p	7g, 72w	55-72	1.6	3.8	72g	1.8	72w
150	100	.3	.4-3	4-19	28-44	72g	72g	72g
150	100p	.8-2.8	6.8	6.8-72	72w	72g	72g	72g

¹ p indicates protected film² g indicates that the film had not been attacked; w indicates that the film wrinkled on removal³ Film appeared unattacked at 72 hours, but failed on removal from the testing reagent⁴ Film became slightly yellow.⁵ Check sample.

TABLE V

Effects of Plasticizers on Benzyl Allyl Starch Films¹

Plasti- cizer	Ratio of Benzyl Allyl Starch to Plasticizer	Curing Time at 150° C. min.	Contact Time (hours) Before Failure ²										
			10% Am- monium Hydrox- ide	5% Sodium Hydrox- ide	5% Phenol	50% Ethanol	4% Acetic Acid	Acce- tone	Soap Solu- tion	Dis- tilled Water	Boil- ing Water	Elonga- tion ³ %	Sward Hardness Number
None		30	4	2	0.8	48	48	1	56-72	48	0.5	> 30	39
Paraplex RG7	1:1	40	.8	.1	.2	72g	72g	.3	8-24	72g	8	> 30	22
	10:3	40	4	.1	.3	72g	72g	.8	48	72g	10	14	42
Duraplex ND75	1:1	40	8-24	1	.3	72g	72g	.3	72g	72g	10	> 30	48
	10:3	40	8-24	1	.5	48	72g	1	72g	72g	4	16	54
Arochlor 1242	1:1	30	2	.1	1	56-72	48	8-24	48	72g	1	22	34
	10:3	40	4	.2	3	48	8-24	8-24	72g	72g	0.2	5	42

¹ Batch 20; 1.70 allyl and 0.44 benzyl groups per glucose unit.² g indicates that the film had not been attacked; w indicates that the film wrinkled but recovered.³ A. S. T. N. No. D-522-41.

TABLE

Effect of the Degree of Cure on Allyl Starch and Benzyl Allyl Starch Films

		Contact Time (hours) Before Failure ²						
Curing Temperature, °C.	Curing Time, Hours	10% Ammonium Hydroxide	5% Sodium Hydroxide	5% Phenol	50% Ethanol	4% Acetic Acid	1% Soap Solution	Boiling Water
Allyl Starch - Batch 51								
100	2.3	0	0	0.2	0.3	7.5-20	1	2-6
100	3	.7	.8	.5	1.1	72g	3	72w
100	4.5	0	.1	.2	2	.4	72g	.4
100	6	.1	.9	9.8-19	9.8	9.8-19	72g	64-72
Min.								
150	10.3	.4	2	2.1	2.1	72g	6	72g
150	20	2.3	17.5-20	7.8-17.5	2-4.3	114g	7-17	114g
150	50	.3	.4	12-22.5	12-22.5	72g	72g	11
150	100	.3	.1	6.2-24	23-29	72g	72g	22-25
Hours								
100	2p	.3	.1	.7	3.2	72g	2.3-72	50-58
100	4.5p	.2	.1	2-6	2-6	2	72g	42-68
100	6p	.2	.5	3.3	1.5	2.7	72g	52-58
Min.								
150	50p	.1						
150	100p	1.5						
Allyl Starch - Batch 52								
Hours								
100	1.3	8.5-18.5	72 ⁴	.3	.8	8.5-72	.2	8.5-72
100	2.3	2.5, 1 ⁵	8.5-18	2.5-8.5	1.7, 1.2 ⁵	2.5-8.5	2.5-8.5	8.5-72
100	4	2.3	2.5-8.5	8.5-18	2.3	2.5-8.5	26.5-42	8.5-42
100	6	.1	.7	2.8	2.8	.8	46-51	1.8
Min.								
150	10.3	.7	4-19	.7	.5	72w	.7	72w
150	20.3	.7	3-18	4	4-19	72g	4-19	.2
150	60	1.9	1.9	4.7	6-72	72g	50-72	.2
150	100	.3	.4-3	4-19	28-44	72g	72g	.2

(CONTINUED)

TABLE VI - continued

Curing Temperature, °C.	Curing Time, Hours	Contact Time (hours) Before Failure ²					
		10% Ammonium Hydroxide	5% Sodium Hydroxide	5% Phenol	50% Ethanol	4% Acetic Acid	1% Soap Solution
100	1p 3	8.5-72	72g ⁶	.5	1.3	72w	18-72
100	2p	8.5-72	26.5-42	2.5-8.5	2.5	2.5	25-72
100	4p	8.5-42	26.5-42	8.5-18	8.5-18	2.5-8.5	8.5-72
100	6p	4.1	6-21	.1	6	30-72	72w
Min.							
150	10p	7g, 72w	55-72	1.6	3.8	72g	72w
150	100p	.8-2.8	6.8	6.8-72	72w	72g	72g
Benzyl Allyl Starch - Batch 46							
Min.							
150	40	73w	5-22	.8	73g	73g	.5
150	70 ³	5-22	.8-1.8	.4	72g	4	6-22
150	90	6-22	.8-1.8	.8-1.8	72g	2.8-72	
150	110	6-22	.5	.5	72g		

¹ p indicates protected film.

² g indicates that the film had not been attached; w indicates that the film wrinkled but recovered.

³ Proper cure, as indicated by spot and knife tests.

⁴ Film appeared unattached at 72 hours, but failed on removal from the testing reagent.

⁵ Check sample.

⁶ Film became slightly yellow.

TABLE VII
Preparation of Benzyl Allyl Starch

Batch No.	Portion of Sodium Hydroxide as Solid %	Temp. °C.	Time Hours	Hydrochloric Acid Used for Breakdown ml.	Substitution Groups per Glucose Unit		
					Benzyl	Allyl	Hydroxy
Flask Batches							
1 ¹	53	97	14	85	.0.60	1.75	0.65
2 ¹	53	97	20	35	.38	1.89	.73
3	53	97	28	60	.31	1.86	.83
4	53	{	80 6.5	25	.35	2.03	.62
			90 19				
			80 1.5				
5	0	{	90 23.5	30	.35	1.89	.76
			90 33.5	50	.55	1.79	.66
			97 32.3	60	.56	1.84	.60
6 ²	0	97					
7 ²	0	97					
Autoclave Batches							
Made with 4 moles of allyl chloride per mole of starch							
8	53	{	80 3.8	50	.47	1.85	.68
			90 22.3	160	.44	1.87	.69
			90 27.8	130	.57	1.69	.74
9	53	90	25	200	.56	1.68	.76
10	12	90	24.8	-	.54	1.66	.80
11	12	90	13.5	-	.54	1.67	.79
11 ³	12	90	35	140	.51	1.65	.84
12	12	90	5	-			
12 ³	12	90					
Made with 3 moles of allyl chloride per mole of starch							
12 ⁴	7	90	18	65	.49	1.60	.91
13 ^{3,4}	7	90	10.8	-	.48	1.58	.94
14 ⁴	7	90	10.8	60	.50	1.70	.80
15 ⁴	7	90	10.5	60	.42	1.70	.88
16 ⁵	19	90	26.5	100	.45	1.74	.81
16 ^{3,5}	19	90	11.5	-	.46	1.75	.71
17 ⁶	0	90	20.5	65	.43	1.75	.81
18 ⁶	0	{	90 6	100	.45	1.74	.81
			110 14				
			80 13.3				
19 ⁶	0	{	90 11.3	70	.51	1.69	.81
			80 13.3	-	.46	1.69	.81
			80 13.3	-			
19 ^{3,6}	0	{	80 5	65	.44	1.70	.81
20 ⁶	0		90 13.5				
			80 5				
20 ^{3,6}	0	{	90 7.5	-	.52	1.64	.81
			80 7.5	100	.38	1.75	.81
			90 23	-			
21 ⁶	0	{	90 2	60	.33	1.77	.81
22 ⁶	0		105 10.5				
			90 3				
23 ⁷	30	{	90 9.5	55	.44	1.70	.81
			110 9.5	-			

(Continued)

TABLE VII - continued

- ¹ Allyl bromide added after 4 hours.
- ² After 8-1/4 hours, 450 ml. of water was removed by entrainment. This process took 11 more hours. Allyl bromide was then added in 200-ml. portions.
- ³ Preliminary sample taken at the time indicated.
- ⁴ Benzyl chloride added after 3-1/4 hours.
- ⁵ Benzyl chloride and the solid sodium hydroxide added after 4 hours.
- ⁶ Benzyl chloride and one-third the sodium hydroxide solution added after 5-1/2 hours.
- ⁷ Benzyl chloride added after 6 hours.

TABLE VIII
Mixed Ethers of Allyl Starch

Batch No.	Substituent (R)	Reagent	Substitution Groups per Glucose Unit		
			R	Allyl	Hydroxyl
24	Ethyl	Ethyl sulfate	0.78	1.77	0.45
25	Ethyl	Ethyl sulfate	.74	1.77	.49
26	Ethyl	Ethyl sulfate	.76	1.73	.51
27 ¹	Ethyl	Ethyl chloride	.42	1.83	.75
28 ¹	Ethyl	Ethyl chloride	.36	1.97	.67
29 ¹	Ethyl	Ethyl chloride	.35	2.10	.55
30 ¹	Ethyl	Ethyl chloride	.32	1.92	.76
31 ¹	Ethyl	Ethyl chloride	.41	1.81	.78
32	Butyl	Butyl iodide	.38	2.38	.24
33	Butyl	Butyl iodide	.83	2.07	.10
34	Butyl	Butyl iodide	.80	2.05	.15
35	Butyl	Butyl iodide	.42	2.38	.20
36	Butyl	Butyl chloride	.39	2.07	.54
37	Butyl	Butyl chloride + sodium iodide	.70	1.95	.35
38 ¹	Butyl	Butyl chloride	.22	2.11	.67
39 ¹	Butyl	Butyl chloride	.26	1.99	.75
40	Amyl	n-Amyl chloride	.20	2.24	.56
41 ¹	Amyl	Mixed amyl chlorides	.42	2.31	.27
42 ¹	Amyl	Mixed amyl chlorides	.23	2.18	.59
43	o-Chlorobenzyl	o-Chlorobenzyl chloride	.54	1.79	.65
44	p-Chlorobenzyl	p-Chlorobenzyl chloride	.58	1.77	.69

¹ Sodium iodide used as catalyst.